Direct Measurement of the Singlet Generation Yield in Polymer Light-Emitting Diodes

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In this study, the singlet and triplet exciton generation yields of a representative blue-emitting conjugated polymer are directly compared using simultaneous optical and electrical excitation measurements. After carefully accounting for bimolecular triplet annihilation and knowing the independently measured solid state inter-system-crossing yield of the polymer, a singlet generation yield of 44% is obtained, in the working device, which is clearly in excess of the simple quantum statistical 25% limit.

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The most important unanswered question in the field of organic light-emitting devices is the physical nature of the spin dependency of charge recombination [1], which determines the singlet formation yield and thus emerges as one of the key parameters that determines the total device efficiency and critically determines which device architecture should be chosen for optimum performance. Quantum mechanical spin statistics predicts that only 25% of charge recombination events will give rise to the formation of a singlet exciton, the rest will be triplet excitons. However, in the case of delocalized excitations on polymers, the recombination could become spin dependent, leading directly to a departure from this limit. Several indirect measurements of this formation ratio have produced widespread values ranging from the spin independent value of 25% up to 95% [2–8]. However, from recent experimental evidence it has become clear that the majority of these earlier measurements on polymers are based on incorrect assumptions or require absolute values of many quantities that are difficult to obtain. For example, the origins of the signals used as the basis of magnetic resonance measurements [2], which initially attracted considerable attention, have been seriously challenged [9]. Other studies have tried to determine the relative singlet to triplet yield by employing emissive acceptors [5,7]. These, however, are not measurements on the pristine polymer either and uncertainties remain as to what extent the inter-system-crossing rate, κ^{ISC}, in such doped systems is still a meaningful constant [10]. Apart from such indirect approaches, experiments that directly probe the two products of the charge carrier recombination, i.e., the singlet and triplet exciton, are generally more convincing and transparent [4]. But again, any attempts to determine absolute values are certainly unrealistic for reasons we shall highlight in the following section [3,6,8]. Instead, relative measurements are deemed to be the superior method and one general approach is outlined as follows.

Generally, we can define two parameters, S and T, to denote any experimentally measurable signals that are *proportional* to the singlet and triplet generation rates whereby each c_i denotes the appropriate constant of proportionality. The superscripts distinguish electrical (el) from optical (opt) excitation. Given that a certain electrical (optical) excitation causes an overall exciton formation I, then the notionally observed signals are given as:

$$S^{\mathrm{opt}} = c_S^{\mathrm{opt}} I_S^{\mathrm{opt}} (1 - \kappa^{\mathrm{ISC}}); \qquad T^{\mathrm{opt}} = c_T^{\mathrm{opt}} I_T^{\mathrm{opt}} \kappa^{\mathrm{ISC}},$$

$$S^{\mathrm{el}} = c_S^{\mathrm{el}} I_S^{\mathrm{el}} \chi (1 - \kappa^{\mathrm{ISC}});$$

$$T^{\mathrm{el}} = c_T^{\mathrm{el}} I_T^{\mathrm{el}} (1 - \chi (1 - \kappa^{\mathrm{ISC}})),$$

with χ being the singlet generation yield. By using the same excitation conditions for the singlet and triplet measurements, i.e., $I_S^{\mathrm{opt}} = I_T^{\mathrm{opt}}$ and $I_S^{\mathrm{el}} = I_T^{\mathrm{el}}$ one can measure T *relative* to S:

$$\frac{T^{\mathrm{opt}}}{S^{\mathrm{opt}}} = \frac{c_T^{\mathrm{opt}}}{c_S^{\mathrm{opt}}} \frac{\kappa^{\mathrm{ISC}}}{(1 - \kappa^{\mathrm{ISC}})}; \qquad \frac{T^{\mathrm{el}}}{S^{\mathrm{el}}} = \frac{c_T^{\mathrm{el}}}{c_S^{\mathrm{el}}} \frac{1 - \chi(1 - \kappa^{\mathrm{ISC}})}{\chi (1 - \kappa^{\mathrm{ISC}})}.$$

In this case neither the driving current, including dark currents, nor the optical excitation dose need to be known. Furthermore, if S^{opt} (or T^{opt}, respectively) is probed under the same conditions as S^{el} (or T^{el}), then $c_S^{\mathrm{opt}} = c_S^{\mathrm{el}}$ ($c_T^{\mathrm{opt}} = c_T^{\mathrm{el}}$) and one measures the electrically excited signals *relative* to the corresponding optical ones:

$$\frac{T^{\mathrm{el}}}{S^{\mathrm{el}}} \Big/ \frac{T^{\mathrm{opt}}}{S^{\mathrm{opt}}} = \frac{1 - \chi(1 - \kappa^{\mathrm{ISC}})}{\chi \kappa^{\mathrm{ISC}}}. \tag{1}$$

Here the absolute value of only one parameter, namely, the inter-system-crossing yield, κ^{ISC}, is required in order to calculate the singlet formation yield, χ. Equation (1) is true for *any* optical excitation combined with *any* electrical one as long as (i) all signals depend linearly on excitation, (ii) the corresponding T and S signals are excited the same way, and (iii) the corresponding el and opt signals are measured the same way. The latter two points are rather mild conditions and can easily be satisfied within a simple experimental layout. The last point, in particular, could be rewritten: the same density of excitons leads to the same signal at the detector. Thus, by no means do we need to count all excitons, for example, the light out-coupling efficiency is no issue here [11]. Also this condition accounts for all exciton quenching mechanisms *as long as*

they apply in the same way for optically and electrically excited excitons. This covers most of the common mechanisms such as quenching at the anodes or impurity sites including the well-known keto defect [12].

However, of most relevance is the first point, an implicit condition that applies to all previous work based on relative singlet and triplet measurements that in fact is not easily satisfied. Recall Eq. (1) holds for any pair of signals, T and S, as long as both depend *linearly* on excitation dose. Clearly, the most natural choice for S is the fluorescence intensity as it is easy to measure and for sufficiently low power depends linearly on excitation dose. But what is a good measure of the triplet signal, T? One may consider transient absorption [4,13] or emission (phosphorescence) detection [4,14]. However, both techniques require rather large excitation densities to yield decent signal-to-noise ratios, which makes migration activated triplet-triplet annihilation (TTA) the major decay route [15,16]. The situation becomes (relatively) worse at higher temperature, because the triplet mobility increases—at room temperature triplet excitons decay essentially only by TTA, i.e., without any phosphorescence emission. This nonlinear loss mechanism for triplet excitons is in fact the reason why many previous studies drastically underestimated the triplet generation channel relative to that of the singlet and thereby obtained excitation dose dependent (interpreted as electric field dependent) singlet exciton generation rates as high as 95% [3–5].

Having concluded that both emission and transient absorption detection are not ideal measurements for the triplet, we still have to rely on them because there are no convincing alternatives. Given this, we need to be aware of the problems associated with this and must account for them in a comprehensive way.

For our measurements we used encapsulated, state-of-the-art diodes based on a blue-emitting polyspirobifluorene polymer (see inset of Fig. 1 for chemical structure [13]), which were mounted in an optically and electrically accessible closed cycle helium cryostat. The triplet accumulation was probed by observing the change in the transient absorption as a function of the time during a 1 ms excitation pulse. Without any alternations in the geometry of the spectrometer, the latter could either be electrically applied using a 100 W current pulse generator, or optically, using a 405 nm laser diode. Additionally, a 780 nm probe beam was focused onto the active area of the device, reflected by the cathode, passed through an appropriate cutoff filter, detected by a 200 MHz transimpedance amplifier, and monitored by a 1 GHz oscilloscope. Up to 1000 excitations were averaged for a single data set with a repetition frequency of only 0.3 Hz in order to allow for sufficient triplet decay between the excitation pulses. The fluorescence level was simultaneously observed by using a second photodiode. Details are given elsewhere [13].

Given in Fig. 1 is a brief spectroscopic characterization of the polymer including absorption, electroluminescence, electrophosphorescence, and excited triplet state absorption. All experiments were performed at 20 K, as this reduces the triplet migration although it certainly cannot avoid triplet-triplet annihilation altogether [16]. Figure 2 shows two typical transient absorption data sets for optical and electrical excitation. Here, we observe the build-in of the triplet excitons as a function of time during a 1 ms electrical excitation pulse. Clearly, TTA affects the observed data, which manifests itself in both the saturation of the induced absorption signal and the rapid decay of the triplet density in the absence of excitation compared to the long radiative lifetime of the triplet exciton, ~1 s [15,16].

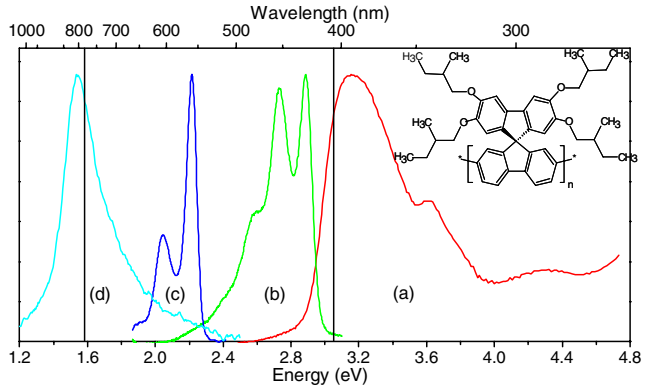

FIG. 1 (color online). A brief characterization of the polymer investigated including absorption (a), electrofluorescence (b), electrophosphorescence (c), and transient triplet absorption (d) spectra. The vertical lines indicate the optical excitation and the transient absorption probe energy, respectively, and the inset shows the repeat unit of the polymer.

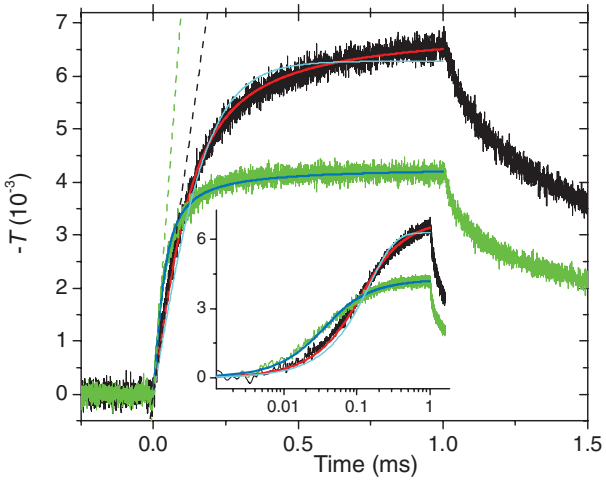

FIG. 2 (color). Representative transient triplet absorption signals during and after a 1 ms optical (black) and electrical (green) pulse as a function of time. The red and blue solid lines are least-squares fits according to Eq. (3); the cyan line is according to Eq. (2). The dashed lines indicate the slopes obtained for this particular data set. In the inset the same data are replotted on a logarithmic time scale.

Therefore, the observed data correspond to the accumulated (integrated) triplet density, limited only by TTA. Clearly, in order to fulfill Eq. (1) one cannot employ the transient triplet absorption intensity at any time after excitation, because there is no regime where the signal depends linearly on time, which in our case parameterizes excitation dose. Instead, a good measure for T is the rise of the time-resolved transient triplet absorption signal at time zero, as here TTA is not yet active. As an alternative to a signal that is proportional to the actual (time-dependent) triplet density, we employ the rate of growth of such a signal, which satisfies Eq. (1), as it is still directly proportional to the triplet generation rate. A straightforward way to acquire this slope, which is completely independent of the exact mechanism of TTA, would be to extrapolate the first derivative of the measured data sets back to zero time. However, given the noise level, it is much more accurate to simulate the experimental data by an appropriate model that accounts for TTA and in that way exploit the *whole* data set. The starting point is the rate equation for the triplet accumulation without the monomolecular decay term, which is legitimate, because the considered time frame (1 ms) is much shorter than the triplet exciton lifetime, ~1 s. If, under certain continuous excitation conditions, the triplet generation rate is I_T then the measured signal intensity is given by

$$\begin{aligned} \frac{dT(t)}{dt} &= \frac{1}{c_T}[I_T - \gamma_{TT} c_T^2 (T(t))^2], \\ T(t) &= \frac{1}{c_T}\sqrt{\frac{I_T}{\gamma_{TT}}}\tanh(t\sqrt{I_T \gamma_{TT}}), \end{aligned} \tag{2}$$

with γ_{TT} being the TTA constant. However, both for electrical and optical excitation the excitons are not homogeneously formed throughout the sample depth. This is obvious for photoexcitation, but also for electrical excitation the dissimilar mobilities of the charge carriers creates a recombination zone near to the electrode that injects the slower moving charges [17]. Given that the triplet excitons are nearly immobile at these low temperatures [16] they cannot compensate for this inhomogeneity by migration. Therefore, in a more realistic scenario, such inhomogeneous excitation is included in the model by using exponential excitation profiles with characteristic inverse thicknesses λ^{opt} and λ^{el}, respectively,

$$\begin{aligned} \frac{dT(x,t)}{dt} &= \frac{1}{c_T}[I_T \lambda e^{-\lambda x} - \gamma_{TT} c_T^2 (T(x,t))^2], \\ T(t) &= \frac{1}{c_T}\frac{2}{ta}\,\mathrm{lncosh}(t\sqrt{I_T a}) \quad \text{with} \quad a = \gamma_{TT}\lambda. \end{aligned} \tag{3}$$

For each data set, both models rely on only two free fitting parameters [$\frac{1}{c_T a}$ and $I_T a$ for Eq. (3)] with $\frac{I_T}{c_T} = \frac{dT}{dt}$ *for* $t = 0$ being the desired quantity. Indeed, accounting for the inhomogeneous exciton generation results in a much improved fit of the experimental data, which can only really be appreciated in the semilogarithmical presentation of the inset of Fig. 2. The instantaneous slope obtained according to Eq. (3) is shown as a dashed line. A more detailed analysis of this model and determination of the charge carrier recombination layer, λ^{el}, in working devices, together with further physical justification of the model, can be found in Ref. [13].

Compared to this rather involved method for the measurement of the triplet excitons, the singlet signal, S, can directly be obtained by measuring the fluorescence levels. Provided the applied electric field strength is sufficiently low ($<6 \times 10^5$ V/cm[22]), then for both kinds of excitation these signals are truly time independent and directly proportional to the singlet generation rates, which is easily shown as the individual optically and electrically excited signals perfectly add up to the simultaneously excited one, i.e., the optically excited fluorescence contribution in the presence of the electrical excitation is unchanged. This proves that for the excitation conditions applied here the singlet exciton is neither quenched by the electric field nor by polarons.

Equation (1) holds true for any combination of optical and electrical excitation dose. Thus, the singlet generation yield could be calculated from a single pair of data sets such as those given in Fig. 2. However, it is more informative to investigate a range of excitation doses. Any nonlinear dependence of T on S [which is not covered by the definitions leading to Eq. (1)] would indicate a nonconstant singlet generation yield, for example, a dependency on driving conditions. Otherwise we could average all the data sets taken at various excitation, i.e., determining the slopes $\frac{T^{\mathrm{el}}}{S^{\mathrm{el}}}(I^{\mathrm{el}})$ and $\frac{T^{\mathrm{opt}}}{S^{\mathrm{opt}}}(I^{\mathrm{opt}})$. In Fig. 3 the experimentally obtained triplet signals under various excitation doses are

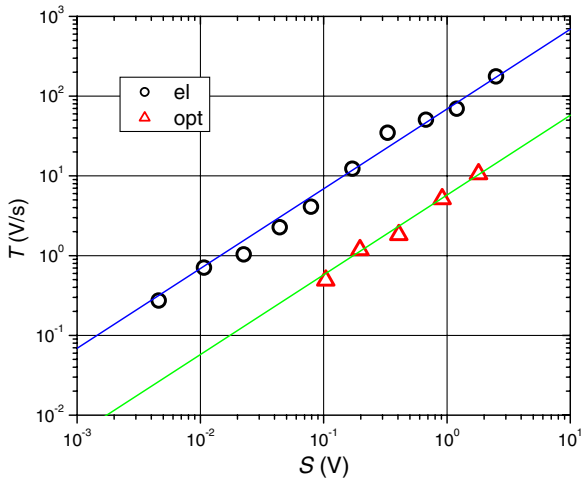

FIG. 3 (color online). Dependency of the rise of the transient triplet absorption signal (T) on its corresponding fluorescence level (S) for electrical and optical excitation on a double logarithmical scale. The two solid lines are least-squares fits of the offset of a strictly linear dependency.

plotted versus their corresponding singlet levels for both excitation modes. 0.3 V/s is approximately the detection limit for the transient absorption, which corresponds to 1.5 mW/cm^2 optical and 5.0 V electrical excitation. On the other hand, the largest optical slope is limited by the maximum available laser power, 30 mW/cm^2. Electrical excitation data are included only up to 7.7 V as for higher voltages effects of sample heating induced by the large driving currents were observed. The graph shows that at the same singlet density about 10 times more triplets are generated for electrical as compared to optical excitation. Critically, both data sets are well described by a linear function with slope of +1 in this double logarithmical presentation which implies that both electrically and optically excited triplet densities depend linearly on their corresponding singlet densities. Thus, the singlet generation yield is a true constant and, in contrast to recent reports [3,4], there is no electric field dependence. In this case we can average our data and the two solid lines are a least-squares fit with only *one* free parameter, which is the offset; the slope was fixed to +1. This yields $\frac{T^{el}}{S^{el}} = 0.069 \pm 0.002$ and $\frac{T^{opt}}{S^{opt}} = 0.0058 \pm 0.0002$ for electrical and optical excitation, respectively, and, consequently, a ratio of 11.9 ± 0.8.

In order to arrive at an absolute singlet generation yield we need to know the absolute triplet formation yield for optical excitation, importantly, at the same experimental conditions, i.e., low temperature and solid state. An exact method to achieve this is the observation of the ground state recovery of the photobleaching where the ratio of the initial transient absorption (all excitons) to the long-lived plateau (any long-lived excitations presumably mainly triplets) directly corresponds to the triplet generation yield [18]. In doing this with sub-pico-second time resolution and very low excitation doses a value of $\kappa^{ISC} = 0.12 \pm 0.02$ is found for polyspirobifluorene in solid state at low temperature, whereby the large error margins cover potential influences from polaron formation, see Ref. [19] for details. Given this, Eq. (1) yields an absolute singlet formation yield of $\chi = 0.44 \pm 0.04$.

We reached this conclusion from directly measuring the relative singlet and triplet populations after charge recombination in a working device. In addition, we avoided the ambiguity of many previous studies that measured triplet quantities, as we did a careful account for TTA. Furthermore, our measurements are also free from other phenomena related to the presence of photo-oxidation products in the polymers or dopants such as heavy metals or heavy metal containing complexes. This result comes from a pure homopolymer and represents the intrinsic polymer singlet formation yield for this polymer. Finally, a singlet generation yield higher than 25% implies it to be a material rather than a generic property. Beyond doubt, the polymer investigated here is not the one with the highest value and a systematic search for better polymers would certainly be worth the effort.

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